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FINAL/REPORT BY J.S. ALABASTER (Water Research Centre)
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FOR M. CARPENTIER - Director General
Environment and Consumer
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EEC Study Contract on Cadmium

Area 4.4 Ecotoxicity of Cadmium

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Final Report

by

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Summary of Report

The literature on the effect of cadmium on aquatic organisms and on biological sewage treatment processes is reviewed. Water quality objectives for the protection of aquatic organisms are tentatively proposed. It is concluded that the effects of cadmium on sewage treatment are of less consequence than possible effects on aquatic life of cadmium remaining in the sewage effluent.

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4.4 ECOTOXICITY OF CADMIUM

4.4.1 Introduction

The presence of cadmium in the environment and its ecological effects have been extensively studied in recent years and several aspects have been thoroughly reviewed, for example, that relating to European freshwater fish (1). The literature that is already adequately covered in this way is not generally dealt with again in detail in this report although the reviews themselves are quoted and, because of the stress laid by the Directorate of Environment and Consumer Protection Service on the need for a critical and thorough review of the literature, some of the more recent references are cited more fully. Several unpublished studies are also referred to. Attention is focused on the freshwater environment as specified by the Directorate, the priority being considered (at the meeting on 3 November 1977) higher for this than for the marine and terrestrial environments. Two aspects are stressed, firstly, the effect of cadmium on aquatic organisms, particularly fish, and secondly, as requested by the Directorate (at the meeting on the 20 April 1977), the effect of cadmium on biological waste treatment processes.

As agreed with the Directorate (at the meeting on 30 January 1978) the effect of cadmium on marine organisms is also dealt with and analytical methods are included in an appendix (Section 4.4.5) but no consideration is given to the effect of cadmium applied to land. Effects on human health are excluded because they have been considered thoroughly by the World Health Organisation whose summary report has been published (74) and whose final report is expected to be published in 1978 (75).

4.4.2 The effect of cadmium on freshwater organisms

Presence of cadmium in freshwater

Cadmium occurs naturally in the environment at geochemically low levels, usually with other metals, principally zinc, and is also present with metals and other chemicals in industrial waste discharges and receiving waters (1). This makes it difficult to distinguish the effects of cadmium *per se* in the aquatic environment and also underlines the need to consider the effect of cadmium in the presence of other substances which may have either antagonistic or synergistic effects on the toxicity of cadmium. Concentrations of cadmium in fresh waters uncontaminated by known sources of the metal are usually between 0.01 and 0.5 µg Cd/l (1). These concentrations are difficult to measure*, as are the higher levels which affect sensitive aquatic organisms; it is also difficult to measure concentrations of dissolved forms of cadmium which are believed to be mainly responsible for the toxicity. Concentrations of cadmium in natural

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* See Appendix (Section 4.4.5)

waters vary and the 95 percentile value over a period of a year or so has been found to be between 2.0 and 2.7 times the 50 percentile value (1). All these factors make it difficult to establish from field observations meaningful relationships between the responses of aquatic organisms and the concentration of cadmium. Cadmium can form a wide variety of complexes with humic material, inorganic ions, and organic chelating agents, but under aerobic aqueous conditions uncomplexed ionic cadmium occurs predominantly, especially in unpolluted soft water of relatively low pH value (1). Cadmium carbonate normally precipitates at pH values greater than about 8.5 but cadmium compounds may also be adsorbed, especially by humic material (1,2,3). For these reasons, and also because data on chemical, physical and biological factors affecting toxicity, particularly water hardness and chemical state, are often lacking, much of the literature is difficult to interpret.

Effect of cadmium on freshwater fish

The relationship between the logarithm of median period of survival of fish and the logarithm of concentration of cadmium in laboratory tests is unusual in that the slope of the line is shallow. Moreover the position of the line varies considerably between experiments (1), possibly because the test solutions have not come to the same chemical equilibrium, different amounts of ionic cadmium being present according to the retention time in the apparatus at the particular pH, temperature and hardness of the water used. It is also possible that the sensitivity of fish to cadmium toxicity may vary with different experimental conditions.

The acute toxicity of cadmium to fish is increased by increase in temperature and by reduction in dissolved oxygen, in water hardness and in pH (1). With hardness the effect is much more marked over a period of 2 to 6 days than it is at 40 to 50 days at which time there may be a clear indication of asymptotic concentrations (1). There are no data on the effect of salinity on the toxicity of cadmium to European freshwater fish but

toxicity might be least at salinities approximately isotonic with the blood of the fish (1). Toxicity is not apparently affected by the presence of suspended humus solids at a concentration of 25 mg/l (1). Acclimation to cadmium may occur in the egg stage (1). Lethal effects may be increased by factors which increase activity such as spawning and the testing of fish in batches rather than singly (1).

Irreversible effects resulting in death may occur after short-term exposure to high, potentially lethal, concentrations of cadmium; in rainbow trout (Salmo gairdneri) they occur within 24 h on exposure to the 48-h LC50 and within 48 h on exposure to the 6-day LC50 (1). There is some evidence that the presence of low concentrations of cadmium, which are not lethal on their own, reduce the time of survival of fish at lethal concentrations of copper and zinc (1). Tests by the Water Research Centre (WRC) with rainbow trout in hard water (4) have shown that the 48-h LC50 for zinc was about 3.8 mg Zn/l in the presence of cadmium at concentrations of up to 2 mg Cd/l and that at lower concentrations of zinc down to 0.5 mg Zn/l, times of survival were accountable by the concentration of cadmium alone.

On the other hand, the lethal effect of low concentrations of cadmium seem to be reduced by the presence of sub-lethal concentrations of zinc (1). In one experiment for example (4), in which rainbow trout yearlings were exposed for four weeks to mixtures of either 30 or 40 µg Cd/l, together with zinc at concentrations of up to 500 µg Zn/l in a hard water (245 mg/l as $CaCO_3$) at pH values of about 7.8, there was a tendency for mortality to be least at intermediate concentrations of zinc, suggesting some antagonism between the two metals.

There is some recent evidence (5) that parasitized fish may be more sensitive to lethal concentrations of cadmium than non-parasitized fish. Three-spined sticklebacks (Gasterosteus aculeatus) were kept in water having a total hardness of 110 to 120 mg/l as $CaCO_3$, pH values at about 8, a temperature of 15°C and concentrations of cadmium in the range 0.5 to 5.0 mg

Cd/l; the median time of survival was between 600 and 900 h for non-parasitized fish and between 300 and 700 h in fish containing the plerocercoids of Schistocephalus solidus at an average of almost $\frac{1}{3}$ of the body weight.

Species differ in their sensitivity to cadmium. Of the species of fish found in Europe and tested to date, the most sensitive appears to be the rainbow trout, long-term experiments on which have shown that adverse effects on reproduction occur at concentrations of cadmium as low as about 2 µg Cd/l in hard water (1). The 'no effect' concentration for this species has not been measured but probably lies between 0.5 and 2 µg Cd/l in hard water.

Adult brown trout (Salmo trutta) appear to be similar to rainbow trout in their resistance to the acute lethal effects of cadmium although as alevins they appear to be slightly more sensitive than rainbow trout (1), and the threshold concentration for median survival is about 10 µg Cd/l and 30 µg Cd/l for the rainbow and brown trout respectively in hard water (1). Moreover, sexual maturity in brown trout has been observed to occur at concentrations as high as 27 µg Cd/l under laboratory conditions (1).

Recently (6) eyed eggs of Atlantic salmon (Salmo salar) were exposed to cadmium in the range 1 to 88 µg Cd/l in a soft water (hardness 12.6 mg/l as $CaCO_3$) at a temperature of 4°C rising to 6 and 8°C after 78 and 97 days respectively, the experiment running for 134 days in all and the pH value being about 6.3. The hatch was virtually complete except at 88 µg Cd/l, where it was 78%, but was delayed slightly (up to 2 days) compared with that of the control (0.3 µg Cd/l); there was a complete mortality of fry at 5 µg Cd/l and higher, and a small (10%) mortality at 1 µg Cd/l compared with 2% mortality in the control.

There are few data on non-salmonid fish and none relate to experiments carried out at more than one hardness for a given species. However, common carp (Cyprinus carpio) appear to be comparable to rainbow trout, whereas goldfish (Carassius carassius) are much less senstive to acutely lethal concentrations, while the long term (40-70 d) lethal values for minnow

(Phoxinus phoxinus), stone loach (Noemacheilus barbatulus), perch (Perca fluviatilis), bream (Abramis brama), and roach (Rutilus rutilus) are much higher than those of trout (1). Embryos and larvae of pike (Esox lucius) and brown trout are comparable in their sensitivity to cadmium. With minnows, however, the lowest concentration at which a significant mortality and spinal deformity occurred was 7.5 µg Cd/l in a soft water having a hardness of 40 mg/l as $CaCO_3$ (1), and with stickle back, Pascoe (7) found 50% mortality among those exposed to concentrations of cadmium in the range 3.2 to 10 µg Cd/l and a median period of survival of 33 d at 1 µg Cd/l in a water having a hardness of 110 to 120 mg/l as $CaCO_3$.

There are almost no data available on the effects of sub-lethal concentrations of cadmium on the behaviour of fish. Hyperactivity has been observed in several species and is associated, especially in males, with increased mortality at spawning time (1).

Field data on the effects of cadmium on fish are scarce. It has been shown by WRC that brown trout were present upstream of an effluent outfall in the River Team, England (hardness 210 mg/l as $CaCO_3$) where the median and 95 percentile concentrations of 'soluble' cadmium over a 44 month period were 2.6 and 6.4 µg Cd/l respectively, but were absent downstream of the outfall where the corresponding values were 7 and 19 µg Cd/l (8). The latter figure is lower than the 8-month LC50 for brown trout (30 µg Cd/l); only small concentrations of other poisons, principally copper and zinc, were also present which, on average, were equivalent to only 0.06 and 0.04 of the respective predicted 48-h LC50 values to rainbow trout. However, on 11 occasions during the study (between 1971 and 1974) samples of water for cadmium analyses were taken by WRC from the river and filtered both on site and in the laboratory and stabilised by the addition of acid; on average the cadmium content of the former were 1.8 times those of the latter (8). Other species which were present under these conditions were bullhead (Cottus gobio), 3-spined stickleback and minnow.

Similar observations (4) have been made by WRC in the head waters of the River Churnet, England, where the median pH value was 7.2, the median hardness was 104 mg/l as $CaCO_3$, and the 50 and 95 percentile values of soluble cadmium, where brown trout and bullhead were present, were 3 and 6 µg Cd/l; median and 95 percentile values of copper and zinc were equivalent to 0.11 and 0.28 respectively of their combined predicted 48-h LC50 values to rainbow trout.

Recent studies in Norway (9) have shown that good brown trout fisheries were present in soft water streams (average hardness between 17 and 20 mg/l as $CaCO_3$) where the median and 95 percentile values of soluble cadmium over the period March-August were about 0.3 and 0.6 µg Cd/l respectively. Good char (Salvelinus alpinus) fisheries were also present in two lakes of similar hardness into which the streams discharged: L. Ringvatnet, where the corresponding percentile values were about 0.6 and 1.4 µg Cd/l respectively and L. Hostovatnet, where they were about 0.5 and 1.2 µg Cd/l respectively. Average concentrations of zinc in the water were up to 35 µg Zn/l in the streams and up to 88 µg Zn/l in the lakes; the corresponding values for copper were up to 43 µg Cu/l for both streams and lakes.

In the R. Thames and its tributaries good or very good populations of brown trout occurred where (in 1975, for example) concentrations of total (not 'soluble') cadmium averaged about 3.5 µg Cd/l, the hardness was about 300 mg/l as $CaCO_3$, and the concentrations of suspended solids were about 11 mg/l (from data supplied to WRC by L B Wood, pers. comm.).

Effect of cadmium on other freshwater organisms

Aquatic invertebrates are generally more resistant than fish to cadmium poisoning although Daphnia and Gammarus appear to be particularly sensitive (1). Immobilization of this organism has been observed after 64 h at 2.6 µg Cd/l in water having a hardness of 100 mg/l as $CaCO_3$ and a temperature of 25°C (10) and Biesinger and Christensen (11) found that the 21-d LC50 was only 5 µg Cd/l, and also showed that at the end of this period at 1 µg Cd/l there was a 7% lower weight than in the controls and that at 0.7 and 0.17 µg Cd/l there was a 50% and 16% impairment of reproduction respectively.

Recent work (12) has shown that within a few months in artificial streams in Georgia, USA, that contained 5 µg Cd/l, the numbers of copepods, ostracods and cladocerans were lower, and the numbers of the protozoan Paramecium bursaria were much higher than those in the controls. Aquatic plants do not appear to be particularly sensitive to cadmium but the absence of data on water hardness generally prevents a comparison to be made with other organisms (1). Thus it is likely that the direct effects of cadmium on fish would be more important than those caused indirectly through reduction in numbers of fish food organisms.

Say (13) demonstrated synergism between cadmium and zinc in their combined effect on growth inhibition of the alga Homidium rivulare, a threshold response being obtained for example at 0.5 plus 0.2 and at 0.1 plus 0.5 respectively of the threshold concentrations of cadmium and zinc; however, the latter were equivalent to 34 µg Cd/l plus 2.5 mg Zn/l in a soft water.

Taub (14) has studied laboratory microcosms comprising the alga (Chlamydomonas reinhardtii), the protozoan Tetrahymena vorax, a rotifer mixture predominantly Philodina, the ostracod Cypridopsis vidua and the bacteria Serratia marcescens kept under static conditions for 5 weeks at an initial concentration of 6.5 µg Cd/l; the main observation was of a small (30%) slightly significant reduction in ostracod population. Information on the water hardness is not readily to hand and concentrations of cadmium were not measured during the course of the experiment. Although the microcosm might demonstrate interaction between different trophic levels it lacks an effective predator.

In another study (15) concentrations of 3 and 10 µg Cd/l were maintained over a 28-d period between April and November in artificial streams containing a soft weir water (hardness about 29 mg/l as $CaCO_3$; pH about 6.5) and significantly reduced the colonisation of tree leaf material by fungi and bacteria and also reduced leaf decomposition compared with a control stream containing 0.02 µg Cd/l; reductions in periphyton biomass and chlorophyll, and in productivity were also observed.

Uptake of cadmium by freshwater organisms

Cadmium has been found to accumulate in the tissues of aquatic organisms exposed to known aqueous concentrations. The concentration of cadmium in the muscle of fish exposed for long periods to low concentrations of cadmium in the water under either laboratory or field conditions is highly variable and can be between 0.1 and 100 times higher (on a wet weight basis) than that in the water, i.e. <0.1 mg Cd/kg muscle (wet weight) in fish from water containing 1 µg Cd/l (1).

Pascoe (7) kept 3-spined stickleback for up to 79 days in solutions containing cadmium in a soft water (hardness 110 to 120 mg/l as $CaCO_3$) and his data show a linear relation between log concentration of cadmium in whole fish (wet weight) and log concentration of cadmium in the water; body residues were about 0.4 mg/kg in fish exposed to 1 µg Cd/l and about 1 mg/kg in those exposed to 10 µg Cd/l. There is, however, no clear general correlation between concentrations of cadmium in the muscle and those in the water to which fish are exposed.

Guppy (Lebistes reticulatus) were fed for 7 weeks on Tubifex worms containing 20 mg Cd/kg without showing evidence of accumulation of cadmium (16); another group exposed for that period to between 70 and 100 µg Cd/l accumulated about 9 mg Cd/kg (wet weight) but there was also no significant difference in cadmium uptake between fish fed cadmium-loaded Tubifex and controls fed normal worms.

Somewhat similar results were found (17) with mosquito fish (Gambusia affinis) kept in flowing water containing 10 µg Cd/l and fed for between 6 and 8 weeks with food flakes spiked with cadmium chloride at a concentration of either 0.1 or 1.0 mg Cd/kg; however, concentrations of cadmium in the fish receiving 1 mg Cd/kg in the food (but not those in fish receiving 0.1 mg Cd/kg) increased significantly from about 0.03 mg Cd/kg to about 0.07 mg Cd/kg (dry weight). Thus food appeared to become a significant source of cadmium only after 8 weeks when more cadmium was accumulated than

was expected by uptake from either water or food acting alone, and may have been the result of physiological changes induced in the fish by the previously accumulated cadmium. Kumada et al. (18) also found that the amount of cadmium accumulated was greater than that from aqueous exposure to cadmium alone when fish were fed with cadmium-contaminated food.

On the other hand Rehwoldt and Karimian-Teherani (19) who fed zebra fish (Brachydanio rerio) over a 6-month period on fish-food spiked with 10 mg Cd/kg (as acetate) and did not expose them to cadmium in the water, found rapid accumulation in whole fish with a levelling-off after a few months to 12.7 and 5.1 mg Cd/kg (dry weight) in females and males respectively.

In a stream studied by Enk and Mathis (20) in which the concentration of cadmium was less than 20 µg Cd/l (on one occasion a concentration of 1 µg was found), concentrations in invertebrates were about 1 mg Cd/kg (wet weight) and in fish and sediments were about 0.13 mg Cd/kg (wet weight) suggesting a concentration factor from food organisms similar to that found by Williams and Gissy (17).

The relative importance of water and food as sources of cadmium to fish may be dependent on many factors such as food quality, relative cadmium concentrations in food and water, the form of cadmium in the water, as well as species of fish.

Summary and conclusions

The data on the toxicity of cadmium to aquatic organisms are not very extensive. Fish, particularly the rainbow trout, have received most attention and the threshold concentrations for median survival at different hardnesses of water and the threshold concentrations for reproductive success in a hard water have been established under laboratory conditions. However, different workers obtain different results under apparently similar conditions. Effects of other environmental variables, especially pH value, temperature and zinc, which are clearly important, are not yet thoroughly worked out. Moreover, the measurement of cadmium, particularly in the dissolved states at concentrations which adversely affect aquatic organisms, has generally been unsatisfactory.

There is need for the development of sensitive methods for measuring soluble cadmium particularly in its ionic forms at the low levels (ug/l) at which it appears to exert its toxic effects on the most sensitive organisms. Relevant environmental variables should also be measured when carrying laboratory toxicity tests and field studies, the latter being particularly important in developing water quality criteria.

Salmon are similar to rainbow trout in their response to acutely lethal concentrations of cadmium in soft water while brown trout are more resistant to adverse effects on reproduction in a hard water. Pike and brown trout are similar in their sensitivity to cadmium at the embryonic and larval stages. Non-salmonid fish appear to be more resistant than salmonid fish to long-term lethal effects in hard water and minnows are more resistant than salmonids to adverse effects on growth in soft water.

Field data are few and relate mainly to brown trout. Thus, any water quality criteria that are developed for cadmium must remain very tentative until further observations are available.

Concentrations of cadmium in fresh water fluctuate seasonally and within shorter time intervals and, in the absence of precise information on the way in which fish populations are likely to be adversely affected by particular levels at certain times of the year, an arbitrary method has to be used to take such effects into account in water quality criteria for fish. One such method is to express water quality as annual 50 and 95 percentile concentrations of 'soluble' cadmium (i.e. that passing through a filter having a porosity of 0.45 µm). Maximum levels of these parameters that appear not to be inimical to fisheries are close to 0.05 and 0.1 respectively of the median threshold concentration for survival, taking into account the effect of hardness of the water. Table 1 shows the values that would probably be appropriate for certain species.

Table 1. Approximate maximum annual 50 percentile concentrations of 'soluble' cadmium (µg Cd/l) tentatively proposed as suitable for freshwater fish throughout their life cycle. Adjustments should be made for the presence of other harmful substances, and low concentrations of dissolved oxygen and sub-lethal concentrations of zinc. The 95 percentile values would be approximately twice the corresponding 50 percentile values

Water hardness (mg/l as $CaCO_3$)	Rainbow trout, common carp and salmon	Brown trout and pike	Perch and minnow
10	0.3	0.6	10
50	0.4	0.9	15
100	0.5	1.0	19
300	0.75	1.5	23

The values in Table 1 should be decreased to allow for low concentration of dissolved oxygen and for the presence of other poisons. The values may also have to be increased to allow for a reduction in toxicity caused by the presence of sub-lethal concentrations of zinc. They may also have to be increased when comparing them with figures for total cadmium because of the proportion that may be present on solids in suspension or may have been 'lost' before analyses were carried out on the water samples.

There is an urgent need for reliable field data from polluted and unpolluted rivers to substantiate the tentative figures given in Table 1.

The few data available on the uptake of cadmium by fish suggest that concentrations in the edible muscle are unlikely to exceed 0.4 mg/kg wet weight in trout exposed to the 95 percentile values appropriate to Table 1. More data are required on other species.

Aquatic invertebrates are generally more resistant to cadmium than fish although certain crustaceans (Daphnia and Gammarus) are especially sensitive, their reproduction being significantly impaired, at least at one particular water hardness under laboratory conditions at a concentration equivalent to the 50 percentile value proposed for rainbow trout in Table 1. In the

absence of experimental evidence and appropriate field observations it might be assumed that the relationship between impairment of reproduction and water hardness is similar to that between the acute LC50 and water hardness, which in turn is similar to that given in Table 1 for permissible concentrations for rainbow trout and hardness. The appropriate 50 percentile values for 'soluble' cadmium for the protection of these crustaceans might therefore be assumed to correspond to those for rainbow trout. These are similar to other criteria that have been recommended (62) where a comparison is possible.

4.4.3 The effect of cadmium on marine organisms

Presence of cadmium in saline water

Concentrations of cadmium in normal sea water range, for example, from 0.032 to 0.075 µg Cd/l (21) or up to 0.11 µg Cd/l (22). Concentrations for the North-East Atlantic Ocean, for example, range from <0.01 to 0.41 µg Cd/l (23), and similar values have been found in the West and South Atlantic Oceans (24,25), and even in the relatively confined Baltic Sea (26) and the Inland Sea of Japan (25). Thus they are generally somewhat lower than that of uncontaminated freshwater (Section 4.4.2). See also reference No. 89.

Apart from natural sources, additional cadmium enters coastal waters as a result of industrial activities such as mining (27), cadmium plating and galvanizing, paint manufacture and from fertilizers (28,29). Thus cadmium contamination of the sea is likely to be most evident in estuaries and nearshore waters of heavily industrialized areas, such as Hong Kong, where values of 50 µg Cd/l have been detected (30).

Behaviour of cadmium in saline waters

The physico-chemical behaviour of cadmium in saline waters has recently been reviewed by WRC (31) but it is not well understood. Formation of a complex may occur with a variety of inorganic and organic ligands, such as those associated with humic compounds; the concentration of some, especially Cl^-, SO_4^- and HCO_3^-, change considerably between the fresh water and marine environments and can lead to increased complexing of cadmium. The presence

of metal-organic complexes in the marine environment has been identified by such workers as Williams (32) and Slowey et al. (33), though the actual form of the complexes, and whether present in a dissolved or colloidal form was not determined. It is clear, however, that they are of great importance to the solubility and oxidation states of cadmium, adsorption of cadmium to other phases, precipitation and transport to the sediments, and to biological productivity (31).

The behaviour of organic materials within sediments and its effect on cadmium are also complex and may play a major role in controlling the mobility of the metal in anoxic sediments and in the overlying water (31).

The distribution of metals between the dissolved and particulate phases is a function of both physico-chemical and biological processes. Three major controlling processes are adsorption (by far the most important); precipitation of insoluble compounds with ions normally present in aerated sea water; and local precipitation of sulphides in reducing environments (31).

For dissolved heavy metals within the estuarine environment there are few unequivocal demonstrations of changes in concentrations in response to anything other than inputs and dilution (31). This is not necessarily because such processes are not occurring, but rather because of the lack of appropriate surveys. However, substantial amounts of cadmium (as well as other metals) have been shown to be released from suspended particulates when they pass into the estuarine environment, e.g. by Nance (34). Also, Holmes et al. (35) have shown that cadmium (and zinc) may be mobilized by changing Eh conditions in sediments. Furthermore, movement of metals from a salt-marsh treated with sewage sludge rich in cadmium has been studied by Banus et al. (36) and considerable amounts of cadmium (and smaller amounts of zinc) were found to be mobilized from the marsh sediments. The mobilization of metals by biological processes may play a very significant role (31).

Wells et al. (37) in a study of the fate of heavy metals from a discharge to a small estuary showed that active immobilization processes must have been removing cadmium (as well as other metals) to the sediments in the vicinity of the outfall, though it was apparently remobilized in the outer reaches of the estuary. The concentration of heavy metals in bottom sediments is determined by processes occurring both before and after deposition, either of which may be of paramount importance. Reynolds and Thompson (38) recorded increased levels of cadmium (as well as of other metals) occurring in the sediments in the vicinity of oyster banks and suggested that heavy metals accumulated in the oysters which on death were incorporated in the sediments. However, a similar feature observed near mussel beds by Hallberg (39) could have been attributable to increased sedimentation of metal-bearing suspended solids.

There is a need for much research on analytical procedures and methodology if even a basic understanding of the behaviour of cadmium in the estuarine and marine environments is to be obtained. It is particularly important to understand more about the factors which govern the concentration and form of cadmium in water and to attempt to ascertain the extent to which it and other relevant substances may be recycled within an estuarine system.

Effect of cadmium on marine organisms

As in the case of cadmium in freshwater the difficulty of measuring low ambient concentrations of cadmium, particularly of the chemical species that are toxicologically significant, and the presence of other contaminants which may have antagonistic or synergistic effects on the toxicity of cadmium, make the interpretation of much of the literature very difficult. Also, many of the experiments carried out under laboratory conditions have utilised unrealistically high concentrations of cadmium for comparatively short periods of exposure. Furthermore, much of the fieldwork has been confined to recording concentrations present without attempting to relate the observations to biological effects (31).

Numerous experiments have demonstrated the acute and chronic toxicity of cadmium to marine organisms and show that some invertebrates (e.g. annelids and crustaceans) are more sensitive than fish. There is evidence that the toxicity of cadmium salts is somewhat less in saline water than in fresh water (40-43) and that the toxicity is increased by reduction in dissolved oxygen and increase in temperature (45).

For several species the relationship between the median period of survival and the concentration of cadmium in laboratory tests, like those for some freshwater fish, such as the rainbow trout, is such that concentrations lethal to fish in 4 days are often one or two orders of magnitude lower than those lethal in 1 day (as shown for example by Eisler's data) (45).

There is some evidence that the presence of low concentrations of cadmium that are not acutely lethal to fish on their own, increase the toxicity of copper and zinc (45).

Although, in general, the eggs and embryos are the most sensitive stages in the life history of teleosts, eggs of marine teleosts have proved to be quite resistant to cadmium as shown by Rosenthal and Sperling (1974) for the herring.

FISH

The 96-h LC50 of the mummichog (Fundulus heteroclitus) has been variously reported as 55 mg Cd/l (43) and 27 mg Cd/l (46) while a concentration of 50 mg Cd/l has caused rapid pathological changes in the intestinal tract and kidney and less rapid changes in the gill (47). However, a concentration of 10 mg Cd/l was not lethal within 10 d (45) although a 10% reduction in liver enzyme activity has been found after 14 days at this concentration (48). At 5 mg Cd/l proliferation of the respiratory tissue and increase in mitotic figures was caused in gill epithelium after periods of exposure of up to about one year (45). Even a concentration of 1 mg Cd/l increased mortality within 96 h when the fish was exposed to copper present in the tests at initial concentrations of 1 and 8 mg Cu/l, or 3 mg Cu/l together with 3 mg Zn/l (45). There are few data for this species at lower concentrations but

adult fish have apparently survived 21 days exposure to 10 µg Cd/l without showing any histological changes in the tissues (29).

The 3-d LC50 for 0-group plaice (Pleuronectes platessa) has been quoted as 7.5 mg Cd/l (73) and in tests carried out over a period of about 19 weeks from August to January by the Department of Agriculture and Fisheries for Scotland (73) in an artificial ecosystem comprising phytoplankton, Tellina and young plaice, there was no adverse effect on the growth and condition of the animals at the highest concentration of cadmium tested (100 µg Cd/l).

The flounder (Pleuronectes flesus) on the other hand showed anaemia, ionic disturbance of the blood and altered carbohydrate metabolism when exposed for 15 d to 100 µg Cd/l when tested at a salinity of 7‰ (50) and showed a decrease in haematocrit and haemoglobin after 33 days exposure to 5 µg Cd/l. However, the hatching rate and viable hatch of the eggs were reduced by concentrations of 2 mg Cd/l and above, at salinities between 16 and 42‰, but this effect was not consistently exacerbated by low salinity (51), unlike the results obtained by Westernhagen et al., 1974 (52) with eggs of herring (Clupia harengus). The latter found a decrease in viable hatch at 1-5 mg Cd/l while Rosenthal and Sperling, 1974 (53) found a reduction in larval size at 1 mg Cd/l in a salinity of 16‰ and additional larval deformity at 0.5 mg Cd/l in a salinity of 5‰.

Eggs of Baltic Sea garpike (Belone belone) incubated at 15°C showed a marked reduction in survival at 2 mg Cd/l and above, especially at the lower salinities of 15 and 25‰, and a significant reduction in viable hatch at 1.0 mg Cd/l and above, especially at salinities of 15 and 35‰ (54); embryonic heart beat and frequency of pectoral fin movement were considerably depressed in prelarvae exposed to concentrations of more than 0.5 mg Cd/l.

Calabrese et al. 1975 studied the American flounder (Pseudopleuronectes americanus) at 25‰ salinity and found inhibition of gill tissue respiration after 80 days at 5 µg Cd/l (87).

Other data for fish relate to the 96-h LC50 which for the armed bullhead (Agonus cataphractus) is 33 mg Cd/l (56) and for the striped killifish (Fundulus majolis) and sheepshead minnow (Cyprinodon variegatus) was 21 and 5 mg Cd/l respectively (43).

MOLLUSCS

In general, judging from acutely lethal concentrations, molluscs are more sensitive to cadmium than fish. The 96-h LC50 values quoted are for the blue mussel (Mytilus edulis), 25 mg Cd/l; eastern mud snail (Nassarius obsoletus) 10.5 (43), which has also shown increased oxygen consumption after 72 h at 0.5 mg Cd/l (57); cockle (Cardium edule) 3.5 (56); and common soft-shelled clam (Mya arenaria) 2.2 (43,57). Butler (1977) also reports the 2, 4 and 7-d LC50 values for the latter as 3.4, 0.85 and 0.13 mg Cd/l respectively (51). The 72-h LC50 for Tellina tenius is 10 mg Cd/l (73). For the eastern oyster (Crassostrea virginica) the 48-h LC50 for the embryo was 3.8 mg Cd/l (54), the 4-8 week LC50 has been reported as 120 µg Cd/l (58), the 8-week LC50 as 200 µg Cd/l (59) and the 15 week LC50 as 100 µg Cd/l (60). This oyster, and the scallop (Aquipectes irradians), both survived exposure to 10 µg Cd/l for 21 days without showing any histological changes in the tissues (49).

CRUSTACEANS

Crustaceans tend to be among the organisms most sensitive to cadmium. The 96-h LC50 values range from 4.1 mg Cd/l for the green crab (Carcinus maenus) to 320 µg Cd/l for the sand shrimp (Crangon septemspinosa) and hermit crab (Pagurus longicarpus) (43). For the latter the 42-d LC50 was about 150 µg Cd/l (from data in reference 62), and at 60 µg Cd/l there was a 40% mortality at 63 days. The 72-h LC50 for Europhnopeus depressus was 4.9 mg Cd/l and decreased oxygen consumption was found in the gill tissue at 4 mg Cd/l (63). The 10-d LC50 of the brine shrimp (Artemia sp.) was 1 mg Cd/l (50) and the 96-h LC50 was 420 µg Cd/l for the grass shrimp (Palaemonetes vulgaris) (43). For the latter the 42-d LC50 was about 400 µg Cd/l (from data in reference 62), there being 10% mortality at 250 µg Cd/l.

Vernberg and De Coursey (1977) have recently summarized (64) work on the effect of cadmium on the fiddler crab (Uca pugilator). The 10-d LC50 for the adult crab was 2.9 mg Cd/l at 30°C and 10‰ salinity (O'Hara, 1973) (42) but was higher (5-7 mg Cd/l) at the optimal temperature and salinity (25°C and 30‰); a concentration of 1 mg Cd/l was not lethal but exposure for 1 h tended to depress respiration rate and, among fish previously acclimated to warm water, to alter the compensatory respiratory response to temperatures below the optimum although the latter effect disappeared with 14 d exposure (64).

Exposure of the zoeal larvae to 1 µg Cd/l for 96-h effectively caused mortality at a narrower range of salinity and at a wide range of temperature than obtained in the absence of cadmium. Even at the optimum temperature and salinity this exposure altered the respiratory rate and tended to decrease swimming activity but did not affect the subsequent survival of the larvae to the megalops stage. Whether or not these effects are relevant to the success of the species in the wild is not known. There also remains the question of whether or not the authors measured the concentration of cadmium during these tests.

Inhibition of reproduction and larval development of Tigriopus japonicus was found after 48 days exposure to 40 µg Cd/l (65). Lobster (Homarus americanus) survived exposure to 10 µg Cd/l for 21 days without showing any histological changes in the tissues (49).

OTHER ORGANISMS

The 96-h LC50 for the sandworm(Nereis virius) and the common starfish (Asterias forbei) was 11 and 0.8 mg Cd/l respectively (43). The 28-d LC50 for the polychaete worms Neanthes arenaceodentata and Capitella capitata were found to be 3 and 7.5 mg Cd/l respectively (72). Another species of polychaete Ophryotrocha diadema, was more sensitive, the 96-h LC50 values being about 4 mg Cd/l (66) and the 17-d LC50 being about 1 mg Cd/l (40); also the population 21 d after the beginning of the period of exposure to

cadmium (the result of survival and reproduction) was about half of that of the controls at a concentration of 2.5 mg Cd/l (66) (from their tables 1 and 2). The 96-h LC50 another polychaete (Ctenodrilus serratus) was also about 4 mg Cd/l and at 0.9 mg Cd/l the population 21 days after the beginning of the period of exposure to cadmium was about half that of the controls (66). These authors also observed enhancement of reproduction in both species at 0.1 mg Cd/l (66).

In two experiments (67), the 11-d threshold concentration for a significant reduction in the growth rate of colonies of the hydroid (Campanularia flexuosa) was 110 and 280 µg Cd/l respectively and the threshold concentration for a significant increase in glucosaminidase activity was 40 and 75 µg Cd/l respectively (68). Effects on the morphology of the hydroid (Eirene viridula) have also been found after 3 weeks at 300 µg Cd/l (69).

The growth of the alga (Skeletonema subsalsum) was inhibited after 20 days exposure to 100 µg Cd/l (70) but in an artificial ecosystem (73) no reduction was found in chlorophyll or in production of phytoplankton at this concentration over a period of 200 days.

The rate of oxygen uptake of mixtures of equal parts of anaerobically digested sewage sludge and artificial sea water was compared with that of controls over a 48-h period (71); the rate was reduced in the presence of 100 µg Cd/l, increased during the last 36 h at 10 µg Cd/l and was not affected at 1 µg Cd/l.

Uptake of cadmium by marine organisms

Exceptionally high cadmium levels in the marine environment are often reflected in the levels accumulated by marine organisms, e.g. up to 81.6 mg Cd/kg in limpet (Patella vulgata) off the Somerset coast (76), up to 178 mg Cd/kg in Littorina sp. from Southampton waters (77), 211 mg/kg in dog-whelk (Nucella lapillus) from the Bristol Channel (78) and up to 34 mg/kg in Tasmanian oysters (Crassostrea gigas) (79). Although organisms have the ability to take up cadmium against the concentration of the surrounding medium (49,80), there is no agreement in the literature on the extent to which those from heavily polluted areas accumulate this metal from the water nor on the relative importance of uptake from food and sediments.

Some field data (e.g. 81, 82) indicate that fish accumulate cadmium in kidney and liver rather than in the muscle and several authors (e.g. 83-86,88) have found quite low accumulation of cadmium by teleosts in the field.

Some organisms such as the polychaete (Nereis diversicolor) appear to regulate their uptake of cadmium (90); for instance, worms from environments high in cadmium possessed a greater regulatory ability than those from an unpolluted one. Such adaption could result in indicator organisms containing lower levels in polluted environments than otherwise might be expected.

Uptake of cadmium is affected by several environmental variables. Nickless et al. (91) have demonstrated variation of cadmium in the limpet (P. vulgata) as a function of its position down the shore line and similar results have been found by others (76). Bryan (92) found seasonal variation in heavy metal concentration in scallops, with lowest values being found in summer, and offered several possible explanations, including higher excretion by the scallops and reduction in dissolved cadmium as a result of uptake by the increased biomass of phytoplankton and chelation by extra-cellular products.

The rate of accumulation of cadmium by the eastern oyster (C. virginica) exposed to a constant concentration in the water, has been studied over a 10-month period under laboratory conditions (93) and found to increase rapidly when the water temperature rose to about 20°C, being, in July and August, about double that in winter and spring.

Salinity as well as temperature has also been shown to be important, an increased uptake of cadmium having been found with the fiddler crab (U. pugilator) at low salinity (42). A similar effect was found by Hutcheson (94) for the cadmium uptake by the blue crab (Callinectes sapidus).

Some authors (e.g. 95) have shown that, in some cases, e.g. the mussel (Mytilus edulis) the concentration of cadmium in the tissues was independent of the size of the individual, although the ratio of cadmium content to body weight varied substantially between different populations, whereas in others, e.g. the Pacific oyster (Crassostrea gigas) (98) and the limpet (P. vulgata) the metal content increased with size (94) and in the latter case was proportional to the square of body weight (95).

The evidence available (e.g. 89) suggests that in general fish accumulate lower concentrations of cadmium than many other organisms and that concentrations are particularly high in crustacea. Laboratory studies (29) showed that concentrations of cadmium in whole organisms exposed to 10 µg Cd/l for 21 days were 2.46, 1.49, 0.72 and 0.48 mg/kg (wet weight)*, in scallops (Aequipectes irradianus), oyster (C. virginica), lobster (Homarus americanus) and killifish (Fundulus heteroclitus) respectively. In an estuar where concentrations of cadmium in shore crab (Carcinus maenus), mussel (M. mytilus), shrimp (Crangon vulgaris) and periwinkle (Littorina littorea) averaged about 1.2, 1.0, 0.6 and 0.6 mg Cd/kg respectively, the maximum concentration in the muscle of eel (Anguilla anguilla), whiting (Merlangus merlangus), flounder (Platichthys flexus) and plaice (Pleuronectes platessa) and whole sprat (Sprattus sprattus) were all lower than 0.4 mg Cd/kg (96). Also, the mean concentrations of cadmium in organisms off the South Atlantic coast were 2.1 mg/kg in the limpet (Patella sp.) and 1.9 mg/kg in the oyster (C. angulata) but less than 0.015 mg/kg in 12 species of fish (88).

The relationships between aqueous concentration of cadmium and concentration in tissues are not well established, even for the common edible species.

Majori and Petronio (1973) kept 2-year old mussel (Mytilus galloprovincialis) for up to 8 days in natural sea water containing a total concentration of cadmium of 0.5 µg Cd/l, and in artificial sea water containing 2.2 and 52.2 µg Cd/l at 21°C and found accumulation factors of 400, 114 and 83 respectively (excluding the shell) i.e. to concentrations of 0.2, 0.25 and 4.3 mg/kg respectively (97). However, Topping (84) found much higher concentrations (112 mg Cd/kg) in Mytilus exposed for 10 months to a slightly higher concentration (100 µg Cd/l), suggesting that such long-term experiments are essential for estimating 'equilibrium' concentrations in such organisms. This conclusion is supported by results obtained with the oyster (C. virginica); at a concentration of 10 µg Cd/l Zisler et al. (1972) found that 21 days exposure resulted in body

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* All concentrations in marine organisms cited in this section are expressed per unit wet weight of tissue.

concentrations of 1.49 mg Cd/kg (29) whereas Zatogian (49) has been reported as having found 18 mg Cd/kg after 4 months exposure between April and August. The latter result is supported by more recent data (93) showing the accumulation of about 13.6 mg Cd/kg in adult (3-year old) oysters exposed to 5 µg Cd/ over a 10-month period between November and August. The concentration of cadmium in the water from which the oysters were taken and in the control solutions was between 0.1 and 0.2 µg Cd/l and the concentration in the oysters was 2.7 mg Cd/kg at the beginning of the experiment and 1.69 mg Cd/kg at the end. These data (43, 93) show that the concentration factor increases with reduction in aqueous concentration of cadmium and appear to be the best available upon which to relate uptake of cadmium from solution to aqueous concentrations of cadmium.

A somewhat similar overall relationship is indicated by the data of Topping (84) for scallops held at 100 µg Cd/l and contained 4.8 mg Cd/kg in the muscle after 4 months exposure, as well as those of Bryan (92) for the scallops Pecten maximus and Chlamys operculatis caught 20 km off Plymouth (where the concentration of cadmium in filtered sea water has been reported to contain 0.06 µg Cd/l), which contained about 4.1 and 0.6 mg Cd/kg respectively.

In the field, however, uptake of cadmium from sediments may also be a relevant factor, as indicated by Ayling (1974) in his study of the Pacific oyster (Crassostrea gigas) at various sites in Tasmania (96); his data show a correlation between concentrations in the sediment and those in the oysters, concentrations of 1 and 4 mg Cd/kg in mud (dry weight) being associated with about 5 and 18 mg Cd/kg respectively in the shellfish. No data, however, are given for salinity or for aqueous concentrations of cadmium.

Summary and conclusions

Data on the effect of cadmium in the marine environment are few and not always consistent so that any conclusions drawn from them must be considered even more tentative than those for the freshwater environment. It is quite clear, however, from laboratory studies that acutely lethal levels of cadmium for adult marine organisms are in the range 1 to 55 mg Cd/l depending upon the

species. Reduction in the viable hatch of fish may also be brought about when the eggs and larvae are exposed to concentrations in the range 0.5 to 5 µg Cd/l.

The adverse effects of acutely lethal concentrations of cadmium are exacerbated by low salinity, high temperature, and low dissolved oxygen concentration but to what extent this obtains for long-term lethal effects or for adverse sub-lethal effects is not known.

The long-term lethal concentration of cadmium for some shellfish, for example the eastern oyster, may be as low as 100 µg Cd/l.

Sub-lethal effects on marine organisms are generally found only at concentrations in excess of 100 µg Cd/l although there are a few notable exceptions, for example, adult flounder (Pseudopleuronectes americanus) which have shown significant changes in the rate of gill tissue respiration at a concentration of about 5 µg Cd/l, and the fiddler crab (Uca pugilator) which has shown an increase in metabolic rate at a concentration of about 1 µg Cd/l. However, whether these effects (or indeed effects on the hatch of eggs and the survival of fry) would have any ecological significance in practice is not known.

There is a dearth of field observations in saline waters that help in establishing water quality criteria for cadmium and marine organisms but one notable study of a simulated simple ecosystem has indicated that over a period of 200 days a concentration of 100 µg Cd/l was not harmful to the organisms involved (phytoplankton, Teilina and juvenile plaice).

Cadmium is accumulated by marine organisms particularly by some commercially exploited species of shellfish and crustacea. Accumulation has been shown to be dependent in some cases upon adaptation of the organisms to high environmental concentrations of cadmium, the size and age of the organism, water temperature and salinity, concentration of cadmium in the water and (probably also) in the mud, and time of exposure. The precise roles of these factors have not yet been thoroughly investigated to the extent that uptake of cadmium by marine organisms could be reliably predicted for field conditions. However, some data suggest that for some bivalve molluscs tissue levels of the order of 10 mg Cd/kg and 1 mg Cd/kg would result from long-term exposure to aqueous concentrations of between 1 and 10 µg Cd/l and between 0.01 and 0.1 µg Cd/l respectively.

4.4.4 The effect of cadmium on biological treatment processes

Recent analyses of Stevenage domestic sewage by the WRC (99) over a period of one month show the mean concentration of cadmium to be 0.0045 mg/l in crude sewage, 0.003 mg/l in settled sewage and 0.002 mg/l in effluent. Higher concentrations would be found in sewage containing industrial wastes (100).

There is little work reported on the effect of cadmium on biological treatment processes and most of it was done 15-20 years ago, when the speciation of metals present in a waste at different pH values was much less well understood.

The inhibitory effect of cadmium has been studied by several workers, using Warburg respirometers. Dawson and Jackson (101) used activated sludge, with a solids content of 3000-7000 mg/l, at 20°C. The presence of 10 mg Cd/l resulted in a 50 per cent reduction in the oxygen uptake. The effect was immediate and persistent. No attempt was made to acclimatise the activated sludge. The authors considered that in practice most heavy metals would be precipitated from the sewage during sedimentation. They also found that manganese, cadmium and zinc when present in pairs caused a larger reduction in oxygen uptake than either metal separately.

Heukelekian and Gellman (102) used Warburg respirometers at 20°C, containing domestic sewage, filtered through cotton wool, and with a BOD of between 200-280 mg/l. The addition of cadmium sulphate at 5 mg Cd/l caused a small but significant reduction in oxygen utilisation; at 25 and 50 mg Cd/l the inhibition of oxygen uptake was greater than 90 per cent for the 5 days of the experiment. Recovery from the initial toxic effects caused by 10-50 mg cadmium/l occurred so that the 5-day BOD was from 78 to 16 per cent of the control oxygen uptake. It was concluded that it is possible to develop a bacterial flora able to oxidise sewage in the presence of increasingly higher concentrations of heavy metals and therefore the toxicity due to a metal ion is not a fixed value because adaptation of the bacterial

seed leads to an increased tolerance. When cadmium was added to mixtures of sewage and activated sludge the toxic effects were found to be less than when comparable concentrations were added to sewage alone and the retarding effect occurred after prolonged periods of oxidation rather than during the initial period.

Burrows (103) used laboratory scale activated sludge plants and measured the inhibitory effect of cadmium on the reduction of BOD of settled sewage from an industrial town. After first obtaining satisfactory treatment, addition of 2 mg Cd/l produced an inhibitory effect and the volume of sewage added to the plant was incrementally reduced, until the BOD of the treated effluent was reduced to 20 mg/l. A period of 10 weeks was necessary for acclimatisation and after 20 weeks of operation the ability of the plants to treat the sewage even in the presence of cadmium improved. The cadmium tended to be removed by the activated sludge.

Maloney, Sheets and Quillen (104) using Warburg respirometers obtained results very similar to those of Burrows. They measured the toxic effect of added cadmium by the amount of inhibition of the oxygen uptake by sewage micro-organisms in the presence of various concentrations of cadmium. They used synthetic sewage prepared from lactose broth and dilution water and seeded with settled sewage. During a 6-day incubation period at 20°, 2 mg Cd/l inhibited the oxygen uptake, but some acclimatisation occurred later though the uptake remained slower than that of the control.

Stones (105) examined the effect of cadmium on the 5-day BOD of domestic sewage. The sewage was diluted one-hundredfold and cadmium sulphate was added at concentrations of up to 10 mg Cd/l. He found that 1 mg Cd/l reduced the BOD by 16 per cent and that 2.3 mg Cd/l reduced it by 25 per cent.

A paper by Pettet (106) is the sole reference to the effect of metals on percolating filters. The BOD and permanganate value of the effluent was only slightly altered in the presence of 104 mg Cd/l added as cadmium sulphate. Nitrification was appreciably depressed by 5.2 mg Cd/l, but at 104 mg Cd/l

the inhibitory effect on nitrification was much smaller, and the author suggested that these results may have occurred because of changes in ambient temperature. With concentrations of 1.0 and 2.1 mg Cd/l in the sewage, concentrations in the effluent were 0.07 and 0.3 mg/l respectively.

Despite the fact that a considerable amount of heavy metal is removed onto the sewage sludge, the only reported work on the effect of cadmium on anaerobic digestion is that of Mosey and Swanwick (107, 108). Cadmium was shown to be a rapid and relatively permanent toxicant to anaerobic digestion. Its inhibitory effect on gas production is a function both of the shock dose concentration and of the contact time. A contact time of only 5 minutes caused detectable inhibition, but an increase of contact time above 12 hours caused no increase of inhibition, hence a shock dose concentration of cadmium is more toxic than the same concentration accumulated gradually (in the latter instance the cadmium will be slowly precipitated, principally as cadmium sulphide). Cadmium toxicity may also be reduced if sulphate is added to a digester some hours before the metal is present. Mosey found the toxicity of cadmium to anaerobic digestion to be dependent on the pH only at values greater than 7. This was attributable to the insolubility of cadmium carbonate.

Mosey, Swanwick and Hughes (103) found that the addition of 28, 56 and 112 mg Cd/l did not result in inhibition of gas production, though 225 mg Cd/l produced an 8 per cent inhibition.

Summary and conclusions

Soluble cadmium salts present in sewage may be precipitated during biological treatment.

If cadmium is precipitated as sulphide or carbonate prior to entry into the digester, cadmium toxicity to the anaerobic treatment process will be reduced.

Soluble cadmium salts are toxic to aerobic sewage treatment processes, 10 mg Cd/l causing a reduction in oxygen uptake of approximately 50 per cent.

Cadmium may have an inhibitory effect on nitrification.

The presence of several heavy metals results in an additive inhibitory effect on sewage treatment processes.

Several of the authors quoted have listed common metals in order of toxicity to aerobic treatment processes. These vary, but cadmium usually occurs around the middle of the list.

Aerobic treatment processes are able to acclimatise to the presence of moderate amounts of cadmium.

When assessing the permissible level of cadmium that may be discharged into crude sewage, the factors to be taken into consideration include the level of cadmium likely to occur in the sewage works effluent, its effect on aquatic life in the receiving stream and possibly the concentration of cadmium and other toxic metals in the sludge, rather than its effect on sewage treatment.

Acknowledgements

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4.4.5 Appendix on analytical methods for cadmium in water

The main analytical techniques used routinely for determining cadmium in natural waters are atomic absorption spectrometry (AAS) using conventional flame excitation (109) and preceded if necessary by solvent extraction and concentration, flameless AAS with graphite furnace (110) and colorimetric methods (e.g. (111)). All should be capable of a detection limit of at least 0.1 µg/l under favourable conditions but normally conventional AAS would be used when the cadmium concentration is at least 5 µg/l to avoid preliminary solvent extraction. Other techniques used have included: ASV (112) which also has a detection limit of approximately 0.1 µg/l but is operationally difficult; neutron activation analysis; X-ray fluorescence; fluorimetry; flame photometry and optical emission spectrometry.

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